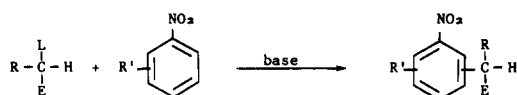


Scheme I



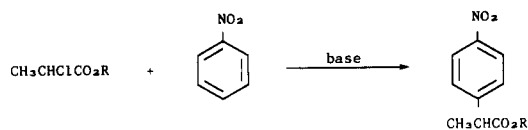
L = leaving group

E = stabilizing group

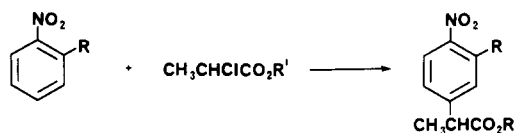
R = H, alkyl

R' = H, halogen, alkoxy, thioalkoxy, aryl

Scheme II



R = alkyl group

Table I. Reactions of Nitroarenes with 2-Chloropropionate Esters^a

R	R'	base	solvent	temp, °C	yield, %
H	Me	NaH	DMF	20-30	66
H	Et	Me ₃ COK	DMF	-5-0	80
Cl	Me	NaH	DMF	25-30	68
Cl	Et	Me ₃ CONa	DMAc	-5-0	83
F	Me	NaH	DMF	0-10	58
F	Me	Me ₃ COK	DMF	-5-0	55
F	Et	Me ₃ COK	DMF	-5-0	75
F	<i>t</i> -Bu	Me ₃ COK	DMF	-5-0	65
OPh	Me	Me ₃ COK	DMF	0-5	56

^a All new compounds gave satisfactory proton magnetic resonance, infrared and mass spectral data and combustion analyses.

propionate and unreacted nitrobenzene. When PTB is used as base only a trace of phenyl 2-(4-nitrophenyl)propionate is observed; the major components of the product mixture are phenol and nitrobenzene. Apparently phenyl 2-chloropropionate is too susceptible to ester cleavage to be used under these conditions.

Although the mechanism of nitroarylpropionate formation is not yet understood, it is reasonable to envision a Meisenheimer salt intermediate of the type suggested by Makosza. We have observed that bases able to remove the acidic proton from alkyl 2-chloropropionates do not necessarily effect alkylation. For example, methyl 2-chloropropionate and nitrobenzene do not react when treated with a mixture of potassium carbonate and a phase-transfer catalyst in DMF, conditions under which the Darzens reaction between this ester and various aldehydes occurs.⁴ This suggests that the pathway may be more complex than rate-determining nucleophilic attack followed by fast elimination of HCl or hydride transfer. Results of further investigations of the mechanism and scope of this useful alkylation reaction are forthcoming.

Registry No. Nitrobenzene, 98-95-3; 2-chloronitrobenzene, 88-73-3; 2-fluoronitrobenzene, 1493-27-2; 2-phoxynitrobenzene, 2216-12-8; methyl 2-chloropropionate, 17639-93-9; ethyl 2-chloropropionate, 535-13-7; *tert*-butyl 2-chloropropionate, 40058-88-6; methyl 2-(4-nitrophenyl)propionate, 50415-69-5; ethyl 2-(4-nitrophenyl)propionate, 50712-64-6; methyl 2-(3-chloro-4-

nitrophenyl)propionate, 24646-28-4; ethyl 2-(3-chloro-4-nitrophenyl)propionate, 50537-08-1; methyl 2-(3-fluoro-4-nitrophenyl)propionate, 86790-39-8; ethyl 2-(3-fluoro-4-nitrophenyl)propionate, 78543-07-4; *tert*-butyl 2-(3-fluoro-4-nitrophenyl)propionate, 88430-80-2; methyl 2-(4-nitro-3-phenoxyphenyl)propionate, 88430-81-3.

Supplementary Material Available: Experimental procedure and spectral and analytical data for methyl 2-(3-fluoro-4-nitrophenyl)propionate and spectral and analytical data for *tert*-butyl 2-(3-fluoro-4-nitrophenyl)propionate and methyl 2-(4-nitro-3-phenoxyphenyl)propionate (2 pages). Ordering information is given on any current masthead page.

G. Patrick Stahly,* Barbara C. Stahly
Kenneth C. Lilje

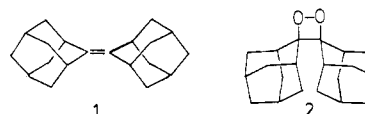
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Electron-Transfer Conversion of Isopropylideneadamantane to its Dioxetane

Summary: Adamantylideneadamantane (1) yields its dioxetane 2 by reaction with ³O₂ and catalytic tris(*o*,*p*-dibromophenyl)aminium hexachloroantimonate (4) at -78 °C in CH₂Cl₂ with a chain length of over 800. Isopropylideneadamantane (5) produces its dioxetane 6 under the same conditions with a chain length of greater than 60.

Sir: Adamantylideneadamantane (1) gives a long-lived radical cation¹ that reacts with oxygen to give a species of greater oxidizing power, causing the characteristic ECE



wave form to be observed in its cyclic voltammogram.^{2,3} The dioxetane 2 is produced in a catalytic reaction for which average chain lengths of 8-24³ and 78⁴ have been reported from coulometry studies of the electrochemically catalyzed reaction. Ando and co-workers⁴ employed other olefins with "protected" alkyl groups (ones that hold the α-hydrogens in the nodal plane of the π system). They showed that the olefin radical cation-³O₂ reaction produces dioxetane nonstereospecifically, in contrast to the dicyanoanthracene-sensitized photochemical reaction, which proceeds by reaction of olefin radical cation with oxygen radical anion. Chemical oxidants also produce 2 from 1 and ³O₂. Use of tris(*p*-bromophenyl)aminium hexachloroantimonate (3) only consumes olefin very slowly, and although NOPF₆ and NO₂PF₆ cause rapid reaction, other products than 2 predominate if enough oxidant is employed to consume 1.² We report here reaction conditions that make the olefin radical cation-³O₂ dioxetane formation synthetically useful, and its extension to an olefin having methyl substitution, showing that "protection" of all alkyl groups is not necessary for efficient dioxetane formation.

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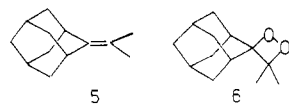
(3) Clennan, E. L.; Simmons, W.; Almgren, C. W. *J. Am. Chem. Soc.* 1981, 103, 2098.

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(4) Gladiali, S.; Soccolini, F. *Synth. Commun.* 1982, 12, 355.

The problem with **3** as a catalyst for the conversion of **1** to **2** is that the electron transfer to generate $1^{\cdot+}$ is endothermic by greater than 7 kcal/mol. Use of tris(*o,p*-dibromophenyl)aminium hexachloroantimonate (**4**)⁵ makes the electron transfer from **1** exothermic by about 1.5 kcal/mol, resulting in much faster reaction than does **3**. Although the chain length for **2** formation (ratio of **2** formed to **4** consumed in the reaction) is only about 10 at room temperature in methylene chloride with oxygen bubbling through it, it rises to over 800 at -78°C . In a preparative run 3.9 mg of **4** (0.5 mol %) in 0.5 mL of CH_2Cl_2 was added to 200 mg of **1** in 50 mL of methylene chloride with oxygen bubbling through it at -78°C . The green color of **4** fades instantly, but the characteristic purple color of $1^{\cdot+}$ ⁶ persists for about 1 min and then fades and is replaced by the green color of **4**. Workup is simple; a few drops of ether destroys excess **4**, and solvent removal gives **2** pure enough for most purposes. A recrystallization from methanol give a 80% yield of pure **2**.

The question of whether unprotected alkyl groups could be present on the olefin was investigated by using isopropylideneadamantane⁷ (**5**). The cyclic voltammogram



of **5** is irreversible at all scan rates in methylene chloride, indicating rapid deprotonation of the unprotected $5^{\cdot+}$. In contrast, employment of 20:1:1 $\text{CH}_2\text{Cl}_2:\text{CF}_3\text{CO}_2\text{H}:(\text{CF}_3\text{CO})_2\text{O}$ that is 0.1 M in tetrabutylammonium tetrafluoroborate lengthens the lifetime enough so that the $5^{\cdot+}$ reduction wave can be seen at rapid scan rates at room temperature. In the presence of oxygen the cyclic voltammogram of **5** shows virtually no current in the $5,5^{\cdot+}$ wave region, as expected for an ECE wave with a much faster radical cation, oxygen reaction than **1** shows. Although electron transfer from **5** to **4** is slightly endothermic (**5** is 0.11 V harder to oxidize than **1** at -78°C), **5** is successfully oxidized to **6** in methylene chloride at -78°C . Runs with a large excess of **5** compared to **4** gave a chain length of about 60, and a preparative-scale reaction (32 mg of **5**) gave an 82% yield of recrystallized **6** (pentane).⁸ **6** has the

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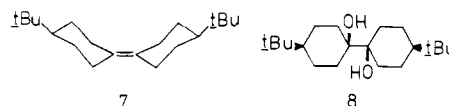
(6) The purple color of $1^{\cdot+}$ persists for tens of minutes at -78°C in the absence of oxygen. We attribute the color to a charge-transfer absorption involving the σ framework interacting with the half-filled $\text{C}=\text{C}$ π orbital. See: Nelsen, S. F.; Kapp, D. L.; Teasley, M. F.; Kessel, C. R.; Grezzo, L. A. *J. Am. Chem. Soc.*, in press.

(7) (a) Woodworth, C. W.; Buss, V.; Schleyer, P. *J. Chem. Soc., Chem. Commun.* **1968**, 569. (b) Meijer, E. W.; Kellogg, R. M.; Wynberg, H. *J. Org. Chem.* **1982**, *47*, 2005. (c) We prepared **5** in 80% overall yield by addition of isopropylolithium to adamantanone (THF, -78°C), followed by dehydration with H_3PO_4 . Landa and Vais (Landa, S.; Vais, J.; Burkhardt, J. *Collect. Czech. Chem. Commun.* **1967**, *32*, 570) report only reduction of adamantanone in ether, but ref 7b claims to have prepared **5** by their method.

(8) A solution of 32 mg of **5** (0.18 mmol) in 12 mL of CH_2Cl_2 (freshly distilled from P_2O_5) was cooled to -78°C ; oxygen was then bubbled through the solution for 20 min. A solution of 5.8 mg of tris(*o,p*-dibromophenyl)aminium hexachloroantimonate (**4**, 0.005 mmole) in 0.6 mL of CH_2Cl_2 was slowly added via syringe. After addition, the green solution

expected spectral properties, melts at $85\text{--}86^{\circ}\text{C}$, and exhibits blue chemiluminescence when heated rapidly to 150°C . Thermal decomposition of **6** gives acetone and adamantanone, and a rate constant of $2.2 \times 10^{-5} \text{ s}^{-1}$ (81°C , 0.016 M **6** in benzene d_6) was measured by NMR integration of the downfield adamantanone and **6** bridgehead hydrogens. The observed ΔG^{\ddagger} (81°C) of 28.4 kcal/mol for **6** is only slightly closer to the extrapolated ΔG^{\ddagger} (81°C) of 25.3 kcal/mol for tetramethyldioxetane⁹ than it is to the 32.8 of **2**.¹⁰ Addition of acid to the methylene chloride increases neither the chain length nor the yield of **6**, so oxygen addition to $5^{\cdot+}$ under our conditions must be more rapid than its deprotonation.

The formation of **6** from **5** is especially significant because $^1\text{O}_2$ fails to make dioxetanes from olefins with unprotected alkyl groups; the "ene" reaction forming allylic hydroperoxides occurs instead.¹¹ For example, Kellogg and Kaiser^{11b} found that **7** gives mostly ene products, al-



though the crude reaction mixture was chemiluminescent upon heating, suggesting formation of some dioxetane. Borohydride reduction gave 5–10% of **8**, the stereochemistry indicating that dioxetane was produced by $^1\text{O}_2$ attack on the face of the olefin which cannot undergo ene reaction due to steric constraints.^{12,13}

Registry No. **1**, 30541-56-1; **1** radical cation, 70535-07-8; **2**, 35544-39-9; **4**, 58047-17-9; **5**, 20441-18-3; **6**, 88510-82-1; **5** radical cation, 88510-83-2; O_2 , 7782-44-7.

was stirred while bubbling oxygen through for 10 min. The reaction was quenched by the addition of 1 mL of diethyl ether and then slowly warmed to 0°C . The organic solution was washed with 5 mL of cold saturated NaHCO_3 solution and dried with K_2CO_3 (15 min at 0°C), and the solvents were evaporated at 0°C with a stream of nitrogen. The resultant yellow solid was recrystallized from pentane at -78°C to give 31 mg of **6** (0.15 mmol, needles, mp $84\text{--}86^{\circ}\text{C}$, 82%); ^1H NMR (CDCl_3) δ 2.69 (br s, 2 H), 1.9–1.7 (m, 6 H), 1.68 (br s, 2 H), 1.60 (br s, 2 H), 1.53 (br s, 2 H), 1.52 (s, 6 H); ^{13}C NMR (CDCl_3) δ 92.9 (C_q), 88.9 (C_q), 36.7 (CH_2), 34.9 (CH_2), 33.3 (CH), 32.3 (CH_2), 26.7 (CH), 26.3 (CH), 23.5 (CH_3); UV (CH_3CN) λ_{max} 293 nm, ϵ 89.

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(12) We thank the Alumni Research Foundation of the University of Wisconsin, the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for partial financial support of this work.

(13) **Note Added In Proof:** Photolysis of an O_2 -saturated CH_3CN solution of **5** (9.8 mM) and 9,10-dicyanoanthracene (0.4 mM) yielded no dioxetane **6**; the only primary photoproduct was the allylic hydroperoxide of the ene reaction (2-hydroperoxy-2-(2-propenyl)adamantane).

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